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TRIBUTYL PHOSPHATE REMOVAL FROM REPROCESSING OFF GAS STREAMS USING A SELECTED SORBENT

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TRIBUTYL PHOSPHATE REMOVAL FROM REPROCESSING OFF-GAS STREAMS USING A SELECTED SORBENT

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Abstract

Laboratory experiments have been conducted to determine the effectiveness of inorganic sorbent materials to remove tributyl phosphate $(C_4H_9O_3)$ PO_4 (TBP) vapors from fuel reprocessing off-gas streams. These experiments used small laboratory-scale columns packed with selected sorbent materials to remove TBP and iodine at conditions approaching those in actual reprocessing off-gas streams. The sorbent materials for TBP removal were placed upstream of iodine sorbent materials to protect the iodine sorbent from the deleterious effects of TBP. Methyl iodide in an airstream containing 30% TBP in normal paraffin hydrocarbons (NPH) and water vapor was metered to two packed columns of sorbents simultaneously (in parallel). One column contained a segment of 8-in. x 14-in. mesh alumina sorbent for TBP removal, the other did not. The measure of the effectiveness of TBP sorbent materials for TBP removal was determined by comparing the iodine retention of the iodine sorbent materials in the two parallel columns.

Experiments using a 18 wt% Ag substituted mordinite iodine sorbent were conducted. Results indicated that the iodine retention capacity of the sorbent was reduced 60% by the TBP and that the column containing iodine sorbent material protected by the alumina TBP sorbent retained 30 times more iodine than the column without TBP sorbent. TBP concentration was up to 500 mg/m^3. Similar experiments using a 7 wt% Ag impregnated silica gel indicated that the TBP vapor had little effect on the iodine retention of the silica gel material. The stoichiometric maximum amount of iodine was retained by the silica gel material.

Further experiments were conducted assessing the effects of NO_2 on iodine retention of this 7 wt% Ag sorbent. After the two columns were loaded with iodine in the presence of TBP (in NPH), one column was subjected to 2 vol% NO_2 in air. From visual comparison of the two columns, it appeared that the NO_2 regenerated the silica gel iodine sorbent and that iodine was washed off the silica gel iodine sorbent leaving the sorbent in the original state.

I. Introduction

Tributyl phosphate $(C_4H_9O)_3$ PO_4 (TBP) diluted with dodecane (or normal paraffin hydrocarbon, NPH) is the solvent extractant commonly used in the PUREX process to separate uranium and plutonium

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from fission products in spent light water reactor (LWR) fuel during the dissolution process. When recycled acid is used in the dissolution process, small amounts of NPH and TBP vapor are released to the off-gas streams, both from the dissolver and the vessel vent. These gas streams contain other airborne fission products released during the reprocessing steps. These airborne fission products need to be removed. Iodine and organic iodides are major radioactive constituents of these airborne products.

Current proposed treatment methods for iodine removal involve the use of silver-loaded inorganic sorbents. European laboratory and pilot-plant studies have shown that the presence of TBP vapor in these gas streams reduce the capacity of the silver beds to remove iodine resulting in more frequent replacement of the silver beds.[1] Studies at the Karlsruhe Reprocessing Pilot Plant (WAK) have shown that airborne TBP in concentrations of approximately 6 mg/ℓ significantly reduced the iodine sorption capacity of AC6120 material. Removal efficiency of AC6120, however, could be restored by introducing NO_2 into the air stream. Dodecane was found to have no deleterious effects.

Very little work has been done in the United States on the problems associated with the TBP contamination of the silver beds. Previous work was reported at the 15th DOE Nuclear Air Cleaning Conference.[2] This work reported on the screening experiments to select candidate sorbents for TBP removal. Continued work in this area involved demonstrating the effectiveness of the TBP sorbents in a simulated off-gas stream. The investigation into air-cleaning processes to remove TBP vapors from fuel reprocessing off-gas streams is described more fully in PNL-2080-18.[3]

This paper focuses on the experiments using a selected solid sorbent to remove TBP upstream of commercial sorbents used to remove iodine from off-gas streams. It also describes the results of an experiment to assess the effects of NO_2 on iodine retention of silver sorbent, which was first loaded with iodine in the presence of TBP.

II. Experiments and Results

A bench-scale demonstration unit was constructed to evaluate the effectiveness of the selected sorbent to remove TBP under conditions approaching those in actual reprocessing off-gas streams (see Figure 1). During experimentation, dry-cylinder air was fed to two, jacketed, gas-washing bottles maintained at 50°C. The constant temperature was maintained by water circulated around the reservoirs of the bottles. The bottles each contained a mixture of water plus 30% TBP in NPH. The stainless-steel lines leaving the bottles were heated to 100°C. Methyl iodide vapor in N_2 was fed to the air stream by a Matheson mass-flow controller, and the entire stream was metered to two columns through Matheson rotameters. The two columns were 2.5 cm in diameter and made of stainless steel. One segmented column was packed with a commercially available iodine sorbent, the other column with two sections of the selected TBP sorbent material followed by two or three segments of the same iodine sorbent as in the other column. The column segments were held together by gaskets and snap joint couplings (see Figure 2 for an example of a column segment). The entire column assemblies were placed in an oven and maintained at 130 to 135°C for all experiments.

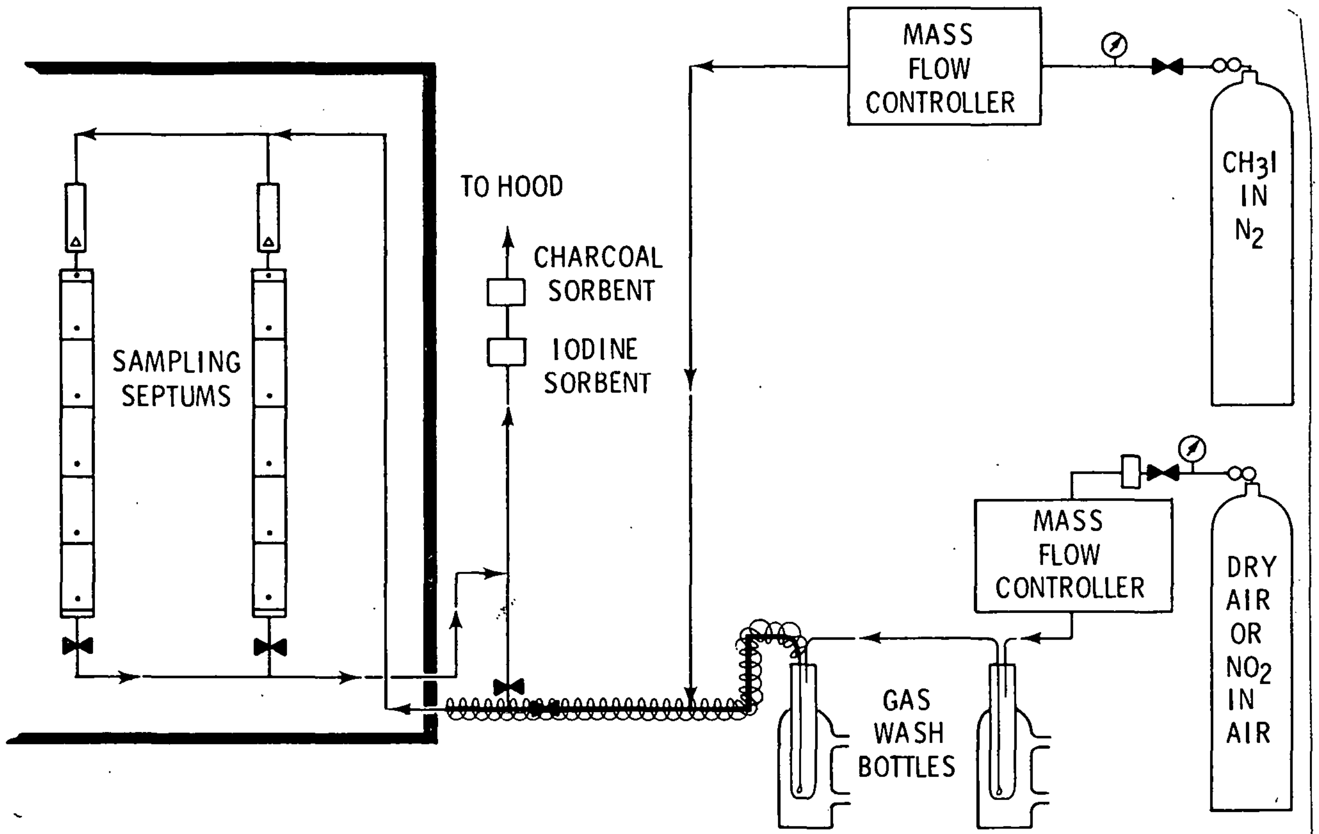

Figure 1. Diagram of apparatus for loading iodine onto selected sorbents.

During an experiment, the breakthrough of methyl iodide, measured by electron capture gas chromatography, was followed in each column segment throughout both columns. Methyl iodide analysis was performed by periodically sampling the feed streams to the columns and downstream of each packed bed segment with a gas-tight syringe through septum sealed sampling ports. The effectiveness of the TBP sorbent materials for TBP removal was determined by measuring the iodine retention of iodine sorbent material. Provisions were made to feed other vapors or gases into the main feed stream.

Evaluation of TBP Sorbent A

An experiment was conducted using the bench-scale demonstration unit to evaluate TBP sorbent A as a sorbent to remove TBP and protect the iodine sorbent beds. Sorbent A is an 8 x 14 mesh granular activated alumina that showed the highest TBP retention of any material examined.(3)

In this experiment, Column I contained two 5-cm segments of material A followed by three 5-cm segments of a commercially available 18 wt% Ag substituted mordenite iodine sorbent. Column II contained four 5-cm segments of the 18% Ag mordenite sorbent. The columns were conditioned with air at 2% relatively humidity for 20 hr followed by 1 hr of conditioning with air plus TBP/NPH vapor prior to metering methyl iodide into the air stream. During the experiment, average airflow was 2 ℓ/min, and average methyl iodide concentration was 160 mg/m^3. TBP vapor concentration was about 500 mg/m^3.

Figure 2. Typical stainless-steel column segment for retaining sorbent materials.

During the experiment, the breakthrough progression of methyl iodide was followed through each segment of the iodine sorbent. This breakthrough is represented as a graph of C/C_o versus grams methyl iodide metered, where C = concentration of methyl iodide leaving a 5-cm column segment of sorbent and C_o = concentration of methyl iodide in the feed stream to the column.

Total methyl iodide metered to Column I was 6.75 g and to Column II 6.11 g. Figure 3 is the breakthrough for sections A, B, C, and D of Column I. Figure 4 is the breakthrough curve for sections A and C of Column II, and Figure 5 is the breakthrough curve for sections B and D of Column II.

To determine the effectiveness of material A to protect the silver mordenite, a comparison of breakthrough curves was made between section C in Column I and section A in Column II and between section D in Column I and section B in Column II. Table I summarizes the breakthrough data.

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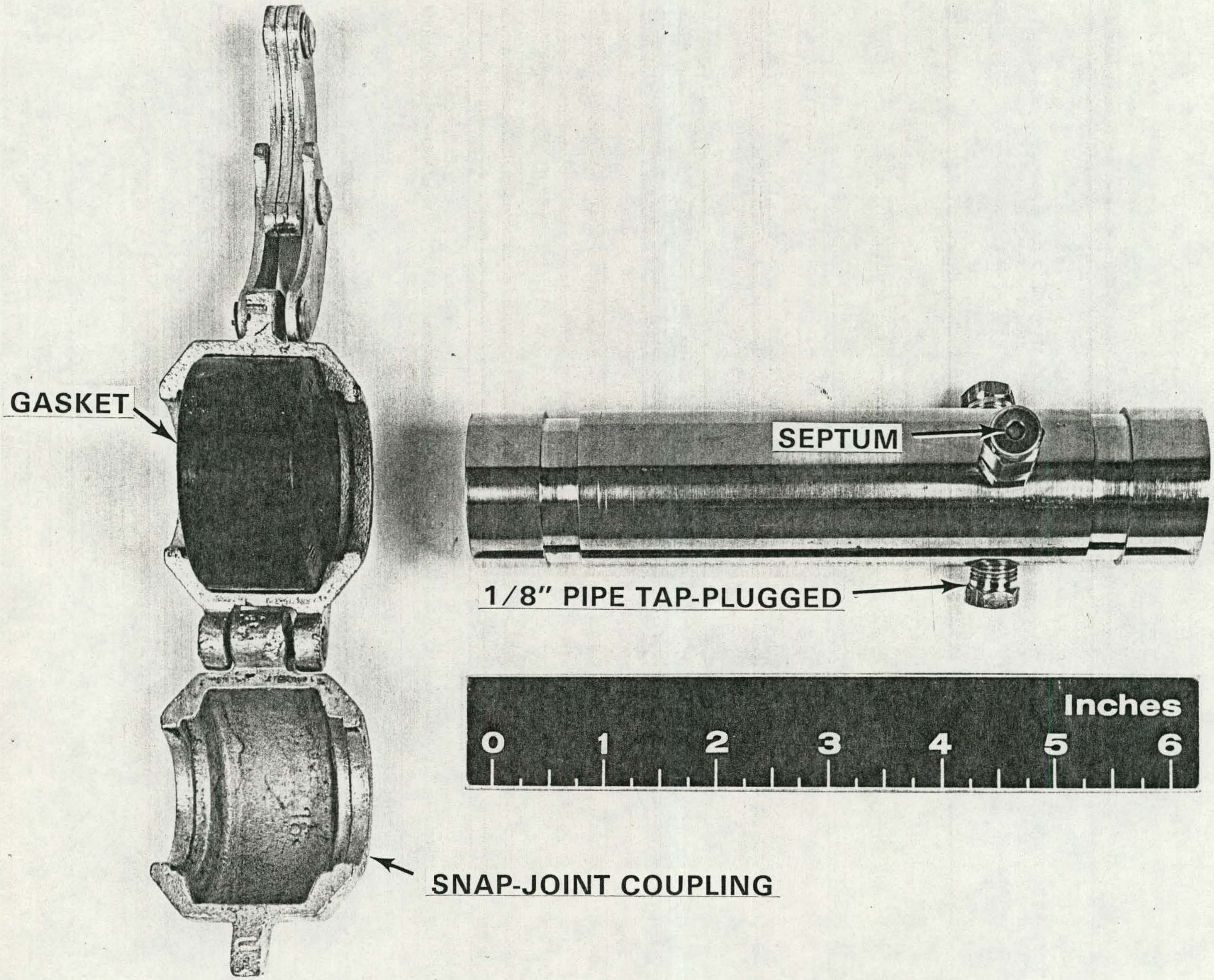
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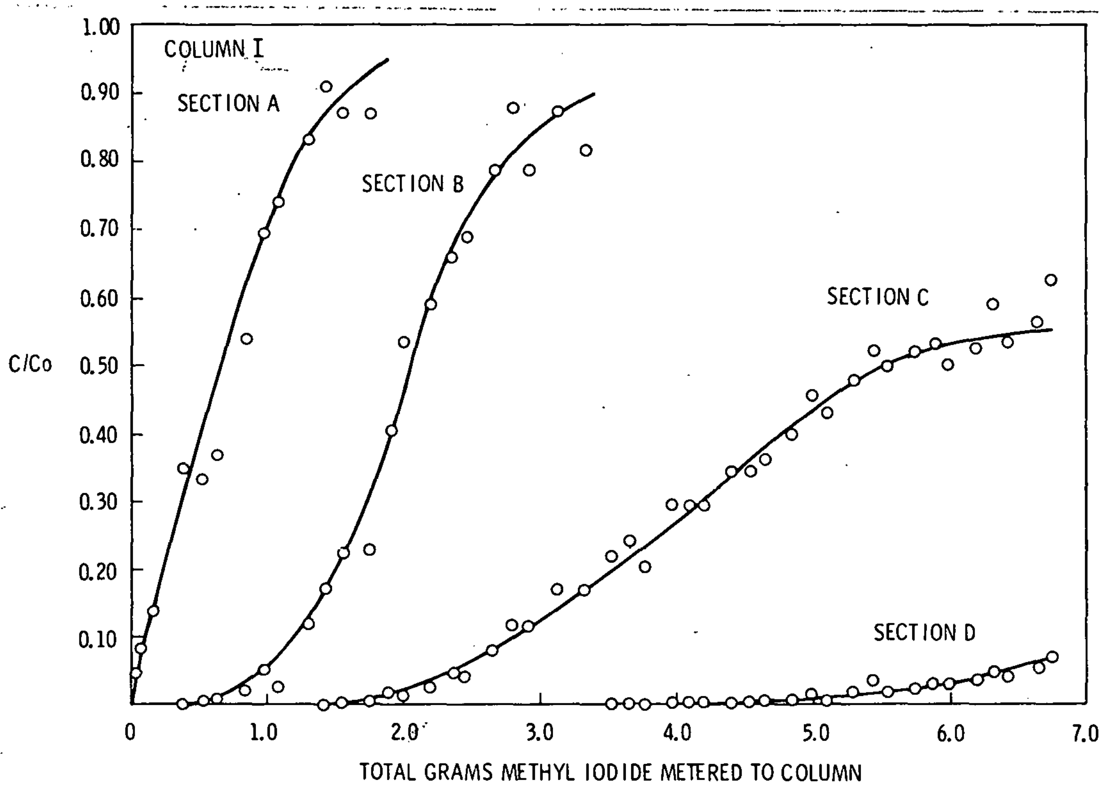

Figure 3. Breakthrough history for methyl iodide loading onto Column I.

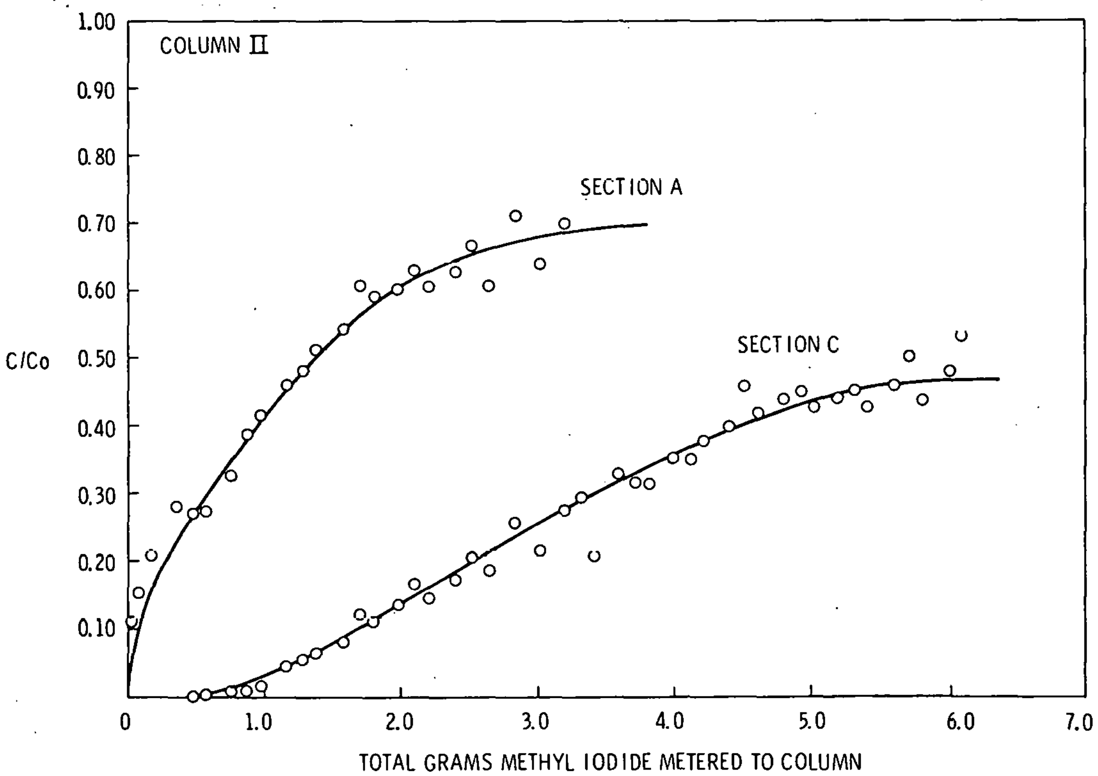

Figure 4. Breakthrough history for methyl iodide loading onto 18 wt% Ag substituted mordenite, Column II, sections A and C.

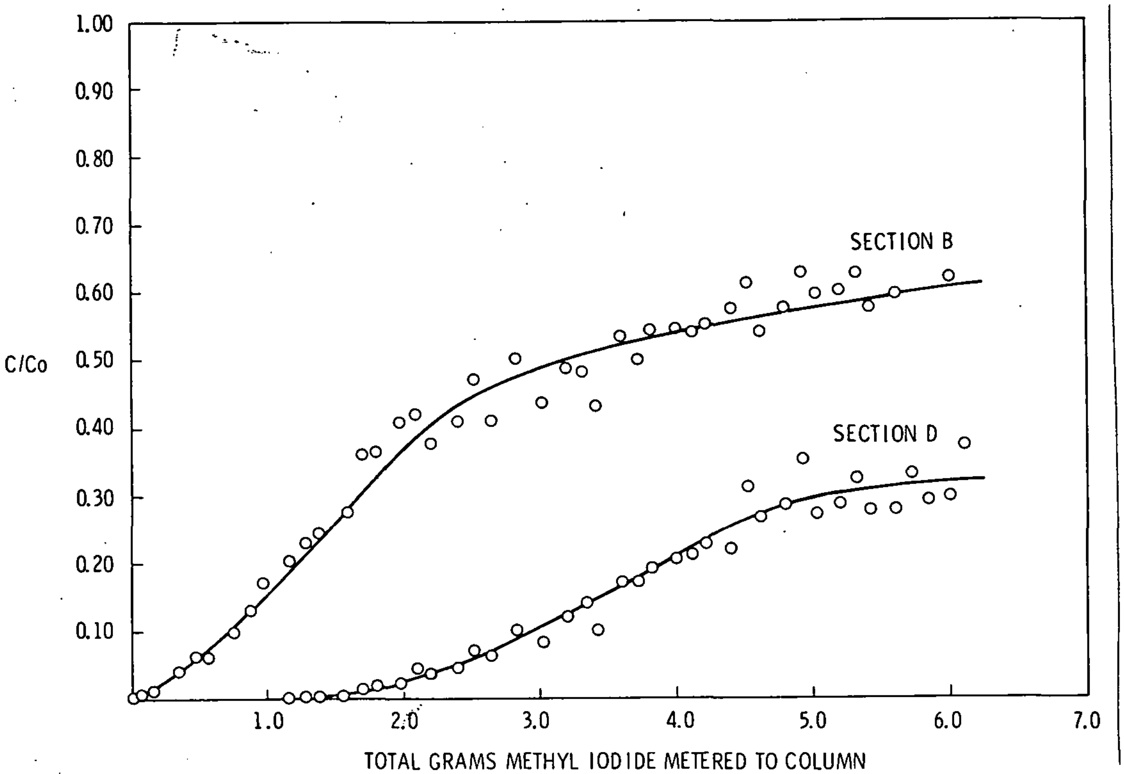

Figure 5. Breakthrough history for methyl iodide loading onto 18 wt% Ag substituted mordenite, Column II, sections B and D.

Table I. Iodine retention of 18% Ag substituted mordenite iodine sorbent.

Sample	Measured % CH_3I Breakthrough (C/C_ox100)	Calculations From Breakthrough Curves* gI/g Ag	Theoretical Maximum** gI/g Ag
Column I			
Section A	90	(1.3)†	
Section B	82	(1.25)†	
Section C	55	0.4	1.2
Section D	7	0.2	
Section E	None	<0.1	
Column II			
Section A	65	0.4	1.2
Section B	60	0.2	
Section C	45	0.2	
Section D	30	0.1	

* Calculated iodine retention at 1% breakthrough in two sections of silver sorbent (from raw data) with uncertainty ±25% at a 95% confidence level: Column I (protection) 4.4 g, Column II (no protection) 0.14 g.
** Based on reaction Ag+I=AgI.
† Grams of Iodine.

The iodine retention at a 1% breakthrough in 10 cm of Column I (sections C and D) was 30 times greater than the iodine retention in 10 cm of Column II (sections A and B). Material A protected the sorbent increasing the iodine retention. The iodine retention of the material was also significantly less than theoretical. The breakthrough for the unprotected Column I, extrapolated to C/C_o = 100%, was ~0.7 g, which is 60% of the theoretical maximum.

It should also be noted that a small amount of iodine was retained by the TBP sorbent in sections A and B of Column I. This was unexpected and is assumed to be adsorption of the iodine onto the TBP sorbent material. This same phenomenon was noted in other experiments.

A second experiment was completed to evaluate material A as a sorbent to remove TBP and protect iodine sorbent beds. Two 2.5-cm dia stainless-steel columns were prepared. Column I contained five 5-cm segments of a 7% Ag impregnated silica gel iodine sorbent, and Column II contained two 5-cm segments of material A followed by three 5-cm segments of the 7% Ag impregnated silica gel iodine sorbent. The columns were preconditioned with air at 2% relative humidity for 20 hr, and air and TBP/NPH vapor for 1.5 hr prior to metering methyl iodide. Conditions for this experiment were air flowing at 1.9 ℓ/min to each column and average methyl iodide concentration of 160 mg/m^3. TBP concentration was about 10 mg/m^3.

At the end of the experiment 8.5 g of methyl iodide had been metered to each column. The breakthrough curves for Column I are given in Figure 6 and Column II are given in Figure 7.

To determine the effectiveness of the TBP sorbent (material A) to protect the iodine sorbent, a comparison of breakthrough curves was made between section A in Column I and section C in Column II, between section B in Column I and section D in Column II and between section C in Column I and section E in Column II. Table II summarizes the breakthrough data.

The iodine retention of the iodine sorbent in sections A and B of Column I and sections C and D of Column II was nearly the same. This indicated that material A contained in sections A and B of Column II had little effect on the iodine retention of the iodine sorbent located downstream. More importantly, however, the data also indicated that iodine retention was near the stoichiometric maximum (within the uncertainty) and therefore the presence of the generated airborne TBP concentration of 10 mg/m^3 did not have a deleterious effect on the iodine sorbent.

Effect of NO_2 on Iodine Sorbent

The final experiment was altered slightly from the previous studies using the bench-scale demonstration unit. In this experiment, the effects of NO_2 on iodine retention were assessed. No protective sorbent for TBP removal was used in this experiment. The protective sorbent was to be included in future studies using NO_2 in the feed stream; however, the project was terminated before additional experiments were started.

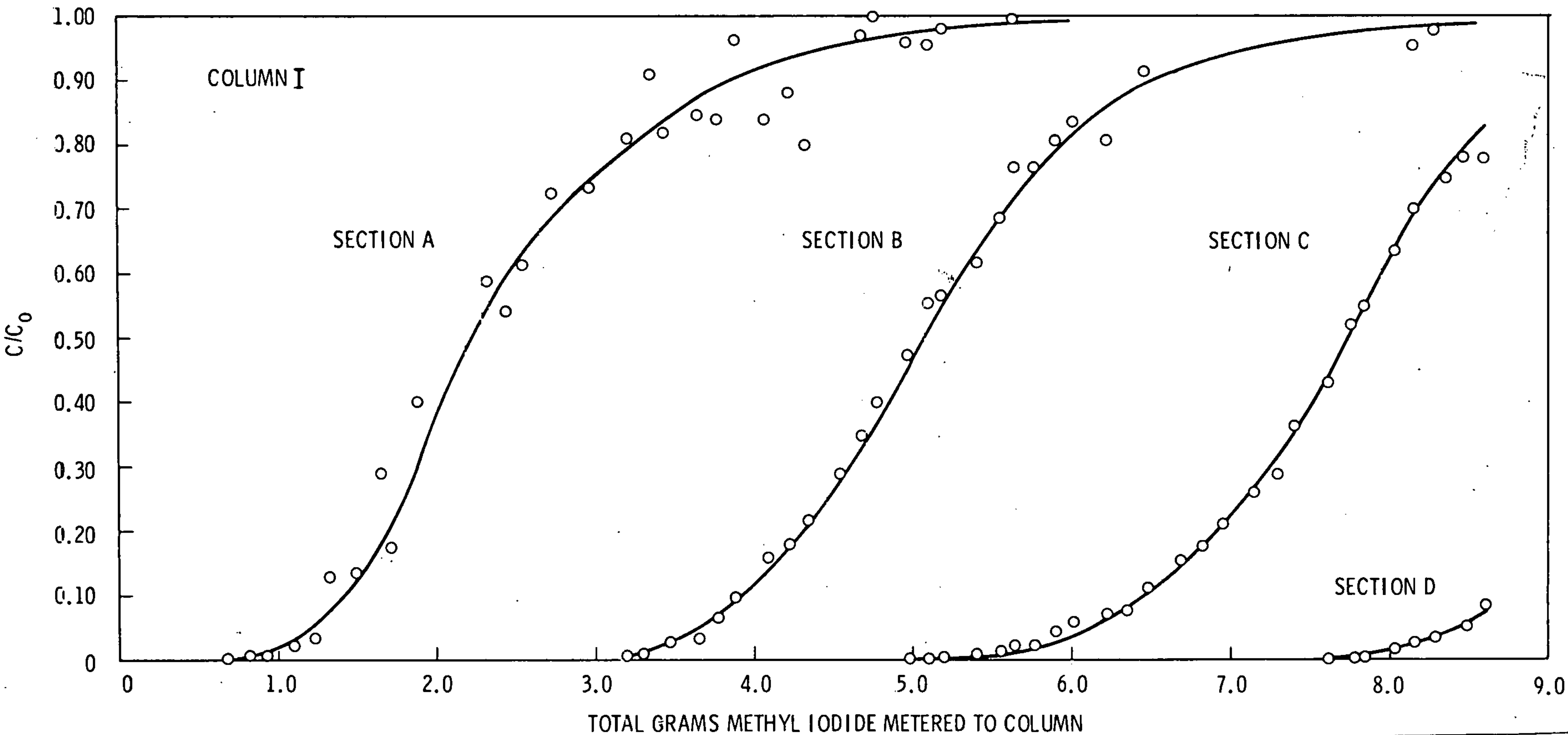

Figure 6. Breakthrough history for methyl iodide loading onto 7 wt% AgI impregnated silica gel sorbent, Column I.

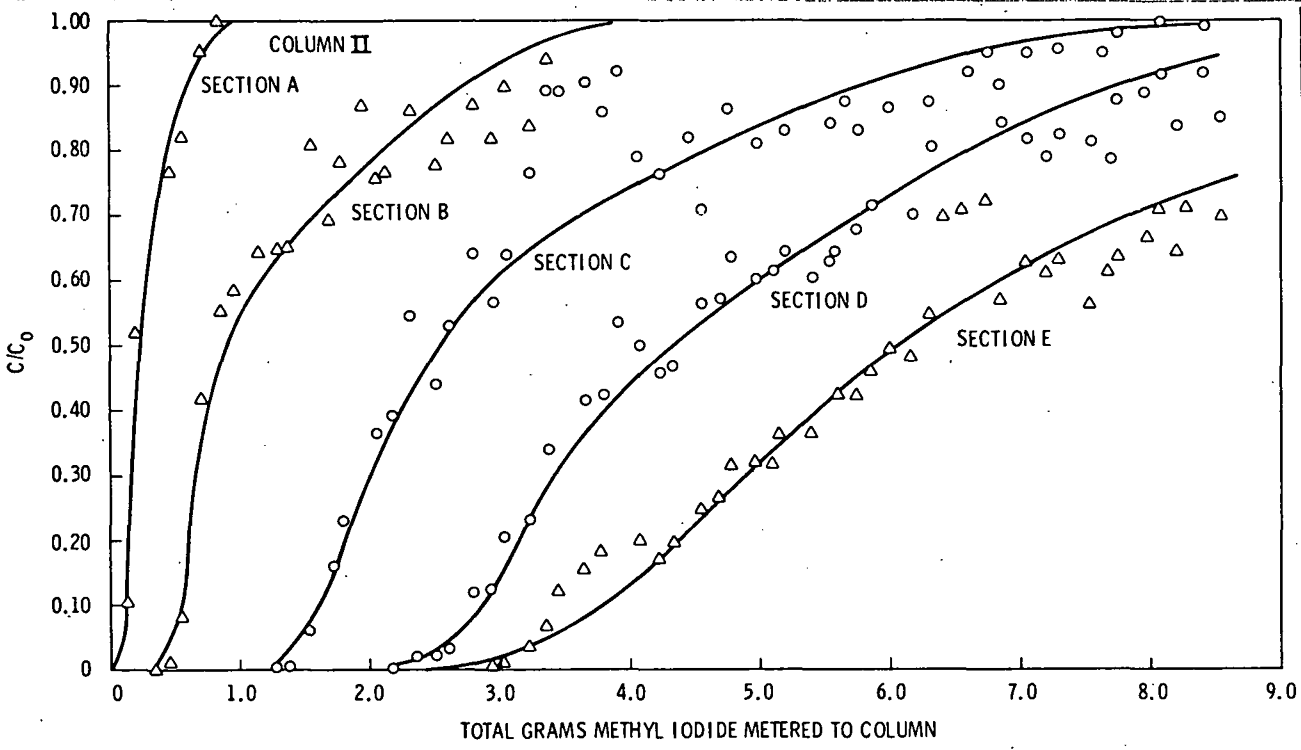

Figure 7. Breakthrough history for methyl iodide loading onto Column II.

Table II. Iodine retention of 7% Ag impregnated iodine sorbent.

Sample	Measured % CH_3I Breakthrough (C/Co x 100)	Calculated CH_3I Retention From Breakthrough Curves* gI/g Ag†	Theoretical Maximum** gI/g Ag
Column I			1.2
Section A	100	1.5	
Section B	98	1.4	
Section C	83	1.3	
Section D	7	0.9	
Column II			1.2
Section A	100 (material H)	(<0.3)‡	
Section B	100 (material H)	(<0.5)	
Section C	100	1.5	
Section D	95	0.97	
Section E	76	0.77	

* Uncertainty is $\pm 25\%$ at the 95% confidence level.
** Based on the reaction Ag + I = AgI.
† Based on 7 wt% Ag.
‡ Grams of iodine.

Two stainless-steel columns were prepared. Both columns contained 5 cm of 7 wt% Ag silica gel iodine sorbent in five segments. The columns were placed in the oven and preconditioned for 24 hr with air at 2% relative humidity and with TBP/NPH vapor for 1 hr prior to metering methyl iodide. The columns were kept at 130° to 135°C throughout the experiment.

Methyl iodide was metered along with TBP/NPH vapor-laden air flowing at 1.95 ℓ/min until a total of 6.66 g was loaded onto each column. The approximate methyl iodide concentration was 200 mg/m^3, and the approximate TBP vapor concentration was 500 mg/m^3.

Breakthrough curves for each column were constructed from the data. Figure 8 is the breakthrough for Column I and Figure 9 is the breakthrough curve for Column II. Iodine retention calculations are given in Table III. As in a previous experiment, the TBP had no effect on the total loading of iodine on the 7% Ag silica gel sorbent even though the TBP vapor concentration was increased from 10 mg/m^3 to 500 mg/m^3. Calculated loading was greater than the stoichiometric maximum in both columns.

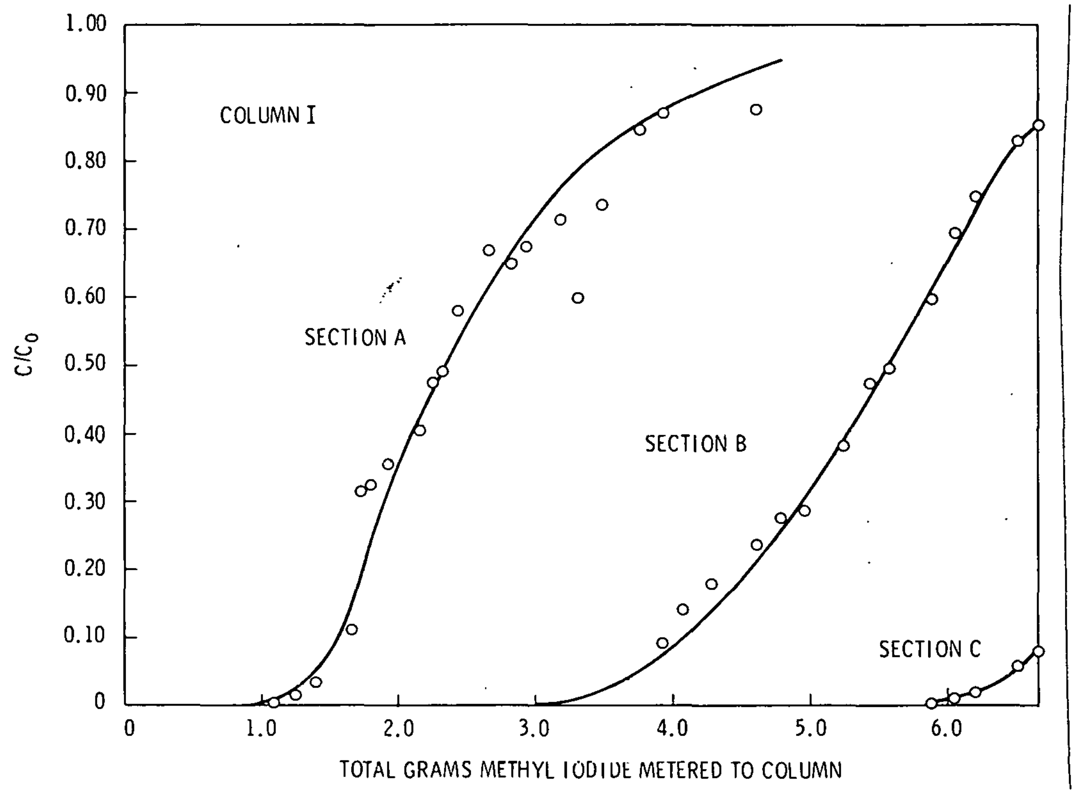

Figure 8. Breakthrough history for methyl iodide loading onto 7 wt% Ag impregnated silica gel sorbent, Column I.

The material from Column I was removed, examined and photographed to note the changes that occurred. The original material was white and beaded. At the end of the iodine loading, the material in the first two 5-cm sections of Column I was a light yellow mixed with a few black beads; the third 5-cm section was about an equal mixture of yellow and grey-black beads; the last two sections were entirely black. This was expected since the first two sections were saturated with iodine and yellow is a characteristic color of AgI. The middle section was only partially loaded with iodine, confirmed by the mix of yellow- and black-colored beads. The last two sections had not "seen" any iodine and were black. The black color is a characteristic of silver oxide formed by reaction of the sorbent with the air or TBP/NPH vapor. The material in all segments was free-flowing and no organic residue could be visually detected, although the odor of TBP was noticeable in all segments.

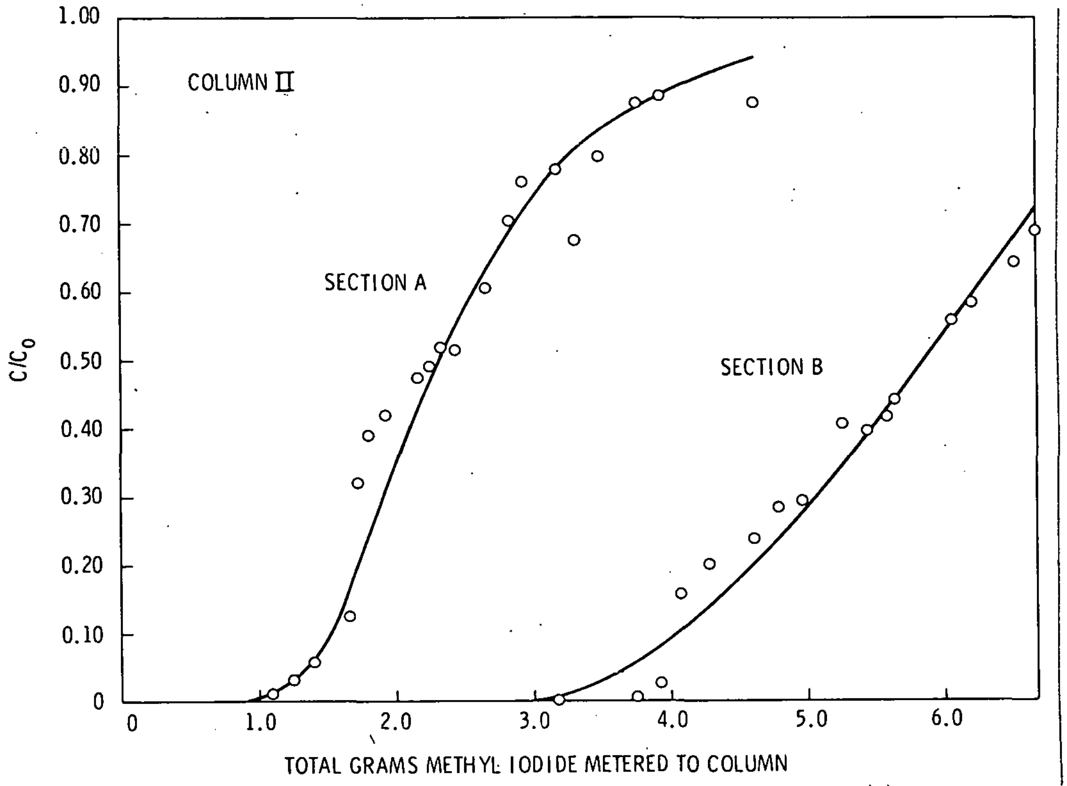

Figure 9. Breakthrough history for methyl iodide loading onto 7 wt% Ag impregnated silica gel sorbent, Column II.

Table III. Iodine retention of 7% Ag iodine sorbent prior to introducing NO_2.

Sample	Measured % CH_3I Breakthrough (C/C_0 x 100)	Calculated CH_3I Retention From Breakthrough Curves* gI/g Ag†	Theoretical Maximum** gI/g Ag
Column I			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		0.7	
Section D	0	---	
Section E	0	---	
Column II			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		1.2	
Section D	0	---	
Section E	0	---	

* Uncertainty is ±25% at the 95% confidence level.
** Based on the reaction Ag+I=AgI.
† Based on 7 wt% Ag.

Column II was left in the oven at 130 to 135°C. Dry air containing ∿2% NO_2 only was then metered to the column at 1.9 ℓ/min for 45 hr. This concentration of NO_2 was in the range expected in actual reprocessing off-gas streams.(4) This process was done to determine the effect NO_2 had on the iodine sorbent after being loaded with iodine in the presence of TBP/NPH. It has been postulated that NO_2 in an air stream containing TBP/NPH will counter-act the deleterious effects of the TBP on the 7% Ag silica gel sorbent by some uncertain mechanism.(1) It was assumed that Column II looked the same as Column I (which was removed) before introducing the NO_2.

At the end of 45 hr the material in Column II was examined and photographed. The first two 5-cm segments were all white and resembled the virgin material. The third 5-cm segment was nearly all white with a thin layer of yellow near the bottom (downstream) of the segment. The last two segments were a pure light yellow; this as noted earlier is characteristic of silver iodide. It appears that the iodine loaded onto the first two segments of Column II was "washed" onto the last two segments of the column by the NO_2, leaving the iodine sorbent in the original white state (regenerated). This was not expected. Rather, it was assumed that the first two segments of Column II would remain loaded with iodine and be the characteristic yellow color. It was also expected that any of the material not loaded with iodine (the material that was dark) would be regenerated to the white color of the virgin material. The silver on the silica gel would be reduced to the ionic (original) $AgNO_3$ state from the oxide (black) state by the NO_2.

III. Conclusions

The following conclusions were drawn from the work reported in this paper.

- The presence of airborne TBP vapor at a concentration of 500 mg/m^3 reduced the capacity of a commercially available 18 wt% Ag substituted mordenite iodine sorbent to retain iodine by 60% (compared to stoichiometric retention). This material could not be used efficiently in actual process off-gas streams without pretreatment to remove TBP. Furthermore, material A was demonstrated to be an effective sorbent for TBP and protect the 18 wt% Ag mordenite iodine sorbent downstream. Protected columns were able to retain 30 times more iodine than unprotected columns.

- A 7 wt% Ag commercial silica gel iodine sorbent was not affected by airborne TBP at ∿10 mg/m^3 concentration. The stoichiometric maximum amount of iodine at saturation (100% breakthrough) was retained by columns of the material kept at 130 to 135°C. In some cases greater than the stoichiometric amount of iodine calculated from breakthrough data was retained by the silica gel sorbent at saturation. Because of this, the iodine sorbent material may be able to be used in actual process streams containing low concentrations (∿10 mg/m^3) TBP without treating the off-gas to remove the TBP.

- Visual examination of 7 wt% Ag sorbent loaded with iodine in presence of TBP/NPH and then subjected to 2 volume % NO_2 in air indicated that the NO_2 will regenerate the sorbent. The iodine appeared to wash off the material and leave the material in the original state. This would be undesirable in an actual process stream containing NO_2. It is necessary to irreversibly trap the iodine in a stable matrix. Additional analytical work is needed to confirm this conclusion.

III. References

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